

NEUTRON-GAMMA TECHNIQUES FOR ON-STREAM ANALYSIS OF COAL

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Rapid analysis of coal is required during buying and selling and for process control of coal preparation plants, coal-burning power stations and coal conversion plants. Modern process control is concerned not only with optimization of process parameters but also with minimization of environmental pollution. The components whose determination is most often needed are calorific value, total ash, moisture content and sulfur content. Other important components include ash fusibility, boiler fouling index, ash electrical conductivity, and nitrogen, chlorine and alkali metals contents.

Process control requires that the analytical result be available within the response time of the process being controlled. For the bulk solids considered here, such times are usually in the range 5 to 50 minutes. Thus, any analysis method, however rapid, is ruled out if it requires sampling and sample preparation times longer than this. Neutron-gamma techniques are non-destructive, non-contact, instrumental methods for elemental analysis of solids and liquids. They are unique in that the analyzed sample volume can be of the order of 30 cm cube. This is because the mean free paths of the incident neutrons and excited characteristic gamma rays in solids and liquids have that order of magnitude. Coal samples of these dimensions can have maximum particle sizes of up to 1 to 2 cm and still be "representative". Therefore sample preparation, if necessary at all, need only take a few minutes. In addition, the methods are amenable to continuous analysis of moving material. Thus even larger amounts of coal can be scanned during a given measurement time with consequent improvement of "sampling statistics".

Since these methods are specific to elements, satisfactory correlation must be assumed or proved between the desired components and the elements determined. Obviously there is no problem with elemental components such as sulfur, nitrogen and chlorine. Calorific value is well correlated with carbon and hydrogen content.⁽¹⁾ Ash content is correlated with the concentrations of the ash-forming elements, the major ones of which are Al and Si.⁽²⁾ Ash fusibility is correlated with the basicity ratio which is a function of the basic and acidic oxides of the ash-forming elements (Al_2O_3 , SiO_2 , CaO , Na_2O , K_2O and to a lesser extent MgO and FeO_x). Moisture is correlated with hydrogen as long as the C/H ratio of the particular coal remains constant.

Early investigations of neutron-gamma methods concluded that, for most key analyses, a neutron generator had to be used as the source and this was not considered practical for plant conditions.^(3,4) Consequently an on-stream coal-ash monitor based on X-ray backscattering, and using a small, sealed radioisotope X-ray source, was developed⁽³⁾ and has been in commercial use for about 10 years. However, the X-ray method is limited to total ash monitoring and the coal must be sampled, dried and crushed to less than about 5 mm particle size before analysis. The availability in 1967 of Cf-252 sealed radioisotope neutron sources rekindled interest in neutron-gamma methods and an on-stream sulfur monitor⁽⁵⁾ and moisture meter⁽⁶⁾ have now been developed to plant prototype stage. Other feasibility studies for multielement coal analysis have been conducted⁽⁷⁻¹⁰⁾ but, to our knowledge, they have each been restricted to consideration of a single neutron-gamma method and have not been able to demonstrate feasibility for analysis of more than a few of the vital elements necessary for proper on-stream analysis of coal.

The studies reported in this paper show that it is possible to determine essentially all of the major and minor elements in coal necessary for process control by not restricting oneself to a single neutron-gamma technique. Furthermore, the optimum nuclear reaction for each element can then be chosen, so reducing the demands

on the gamma-ray detector and electronics. This in turn makes possible the use of the simplest and most practicable instrumentation for reliable plant operation.

NEUTRON-GAMMA METHODS AND INSTRUMENTATION

Methods

In neutron-gamma methods of analysis neutrons from a suitable source bombard the sample, exciting nuclear transitions. Excited nuclear states decay at once with emission of "prompt" gamma rays whose energies are characteristic of the excited nucleus and whose intensities are proportional to source strength, element concentration and spectrometer efficiency, as in other methods of spectral analysis. If the sample and source are separated, the prompt gamma-ray emission stops but "delayed" or "activation" gamma emission is usually still present. The intensity of the activation gamma rays is, as before, proportional to element concentration but also falls off exponentially with time according to the half-life of the product nucleus. The incident neutrons can have any energy from several MeV ("fast" neutrons) to less than 0.1 eV ("thermal" neutrons). Fast neutrons excite several useful reactions and thermal neutrons excite several others. So in practice we can speak of four types of neutron-gamma analysis: (1) fast neutron-prompt gamma; (2) fast neutron activation; (3) thermal neutron-prompt gamma; and (4) thermal neutron activation.

Although the cross sections for producing prompt gamma rays are relatively high, yielding large signals, their detection must take place in the presence of a high background from the nearby neutron source. The design of a practical prompt gamma-ray analysis system is, therefore, a compromise between high detector background and geometrical losses due to the bulky neutron and gamma-ray shielding required. The main advantage of neutron activation is that the source and sample can be separated, enabling the signal to be measured at low background. Activation gamma spectra are also less complex. The cross sections for activation gamma emission are generally lower than those for prompt gamma emission but the much lower background outweighs this, resulting in activation often being the preferred reaction if a choice exists. Table I lists the main characteristics of the preferred methods for analysis of the important elements in coal.

Instrumentation

A neutron-gamma analyzer consists essentially of a neutron source, a gamma-ray spectrometer and a sample presentation system. Instrumentation suitable for in-plant operation must be ruggedly constructed and packaged, and must be capable of operating reliably over long periods, unattended. It should, therefore, be as simple as possible, use solid state circuitry in preference to vacuum tubes, have the minimum number of moving parts, avoid vacuum systems and ultra-high voltages, and operate without the need for special supplies such as liquid nitrogen, cooling water and compressed air.

Three types of neutron source exist, nuclear reactors, neutron generator tubes and radioisotope sources. Radioisotope sources have advantages of small size, rugged, solid state construction and stability of output. However, their steady decay has to be corrected for and forces renewal after about two half-lives. Also they cannot be "turned off" and they provide a potential radioactive contamination hazard in the event of an accident. Since Cf-252 sources have withstood being dropped 20,000 feet down a borehole and fished out without developing radioactivity leaks, we feel that the combined probability of an accident plus serious contamination is very low. Since it will be shown that the required analyses can be performed using relatively low neutron outputs ($< 10^9$ /sec) the need to "turn off" the sources doesn't arise. Only 1 or 2 feet of biological shielding is required for neutron sources of this strength and they can be handled for short periods without any shielding, using the proper tools. As for the radioactivity induced in the sample

TABLE 1

PREFERRED NUCLEAR REACTIONS FOR IMPORTANT ELEMENTS IN COAL

Element	Nuclear Reaction	Threshold Neutron Energy	Main Gamma Energies (MeV)	Half Life
Hydrogen	(n,γ)	Thermal	2.23	Prompt
Carbon	(n,n'γ)	4.8 MeV	4.43	Prompt
Nitrogen	(n,γ)	Thermal	10.83, 10.32	Prompt
Sodium	$^{23}\text{Na}(n,p)^{23}\text{Ne}$	3.75 MeV	0.44	38 sec
	$^{23}\text{Na}(n,\gamma)^{24}\text{Na}$	Thermal	1.37, 2.75	15.0 hrs
Aluminum	$^{27}\text{Al}(n,p)^{27}\text{Mg}$	1.9 MeV	0.84, 1.01	9.5 min
	$^{27}\text{Al}(n,\gamma)^{28}\text{Al}$	Thermal	1.78	2.31 min
Silicon	$^{28}\text{Si}(n,p)^{28}\text{Al}$	3.96 MeV	1.78	2.31 min
	(n,n'γ)	1.9 MeV	1.78	Prompt
Sulfur	(n,γ)	Thermal	5.42	Prompt
Chlorine	(n,γ)	Thermal	6.11	Prompt
	$^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$	Thermal	1.64 and 2.17	37.3 min
Potassium	^{40}K	Natural	1.46	1.3×10^9 yr
Radioactivity				
Calcium	$^{48}\text{Ca}(n,\gamma)^{49}\text{Ca}$	Thermal	3.1	8.9 min
Titanium	$^{50}\text{Ti}(n,\gamma)^{51}\text{Ti}$	Thermal	0.32, 0.93	5.8 min
Manganese	$^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$	Thermal	0.85, 1.81, 2.1	2.58 hrs
Iron	(n,γ)	Thermal	7.63	Prompt
	(n,n'γ)	0.86 MeV	0.84	Prompt

by neutron irradiation, it is both short-lived and completely negligible, being a few orders of magnitude lower than can be detected by a dose rate meter and of the same magnitude as natural K^{40} radioactivity. Two sources were used in the present study, a ^{38}Cl $\text{Pu}^{238}\text{-Be}$ fast neutron source (half-life 86 yrs) and a moderated, $100\text{ }\mu\text{g}$ Cf^{252} thermal neutron source (half life 2.6 yrs).

The second major component of an analysis system is the gamma-ray spectrometer which consists essentially of an energy-dispersive gamma-ray detector, HV supply, pulse amplifiers, an analog-to-digital converter, and a multichannel analyzer with microcomputer for spectrum acquisition and data analysis. High resolution, liquid nitrogen cooled $\text{Ge}(\text{Li})$ gamma-ray detectors have been proposed for coal analysis and can resolve even the most crowded gamma spectra. However, these detectors are relatively easily and permanently damaged by neutron absorption or loss of cryogenic cooling. Also their gamma-ray detection efficiency is an order of magnitude lower than that of the more rugged $\text{NaI}(\text{Tl})$ detector and they cannot operate at count rates above about $10^4/\text{sec}$ without severe resolution degradation or signal losses due to dead time. Scintillation counters using $\text{NaI}(\text{Tl})$ crystals (or $\text{CsI}(\text{Na})$, $\text{CsI}(\text{Tl})$, $\text{CaF}_2(\text{Eu})$, etc.) do not require cooling or vacuum and are available in large sizes suitable for efficient gamma-ray detection. They can operate at count rates up to about $10^5/\text{sec}$ without special electronics ($10^6/\text{sec}$ with special electronics). They are little affected by neutrons and the effects (induced radioactivity) are reversible and do not seriously hinder operation. The crystal-photomultiplier assembly must be temperature controlled to about $\pm 1^\circ\text{C}$ and not subjected to thermal shock. The gamma-ray energy resolution (in the range 5 to 8%) is adequate to resolve most gamma energies of interest. All the experiments reported here were conducted with a $\text{NaI}(\text{Tl})$ detector and standard electronics, a schematic of which is shown in Figure 1. Figure 2 shows a schematic of one measuring head indicating the relative position of source, sample, detector and shielding. Figure 3 shows a photograph of a typical measuring head and the electronic system suitable for operating three such heads. A minimum of three heads would be required if all four neutron-gamma techniques were needed for a particular multielement analysis.

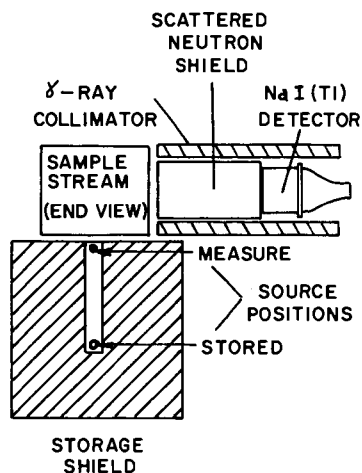
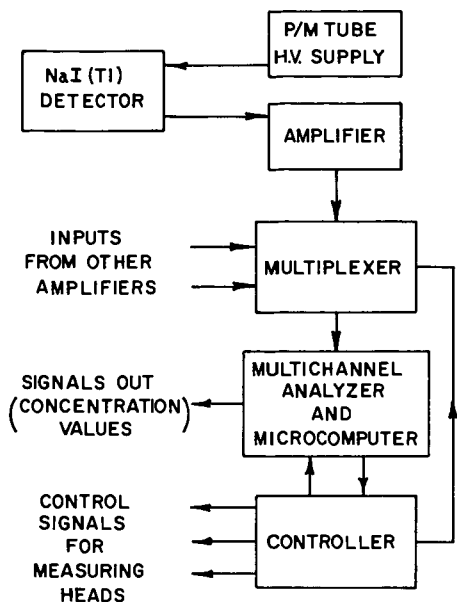


FIGURE 1 SIMPLIFIED ELECTRONIC SCHEMATIC

FIGURE 2 SCHEMATIC OF MEASURING HEAD

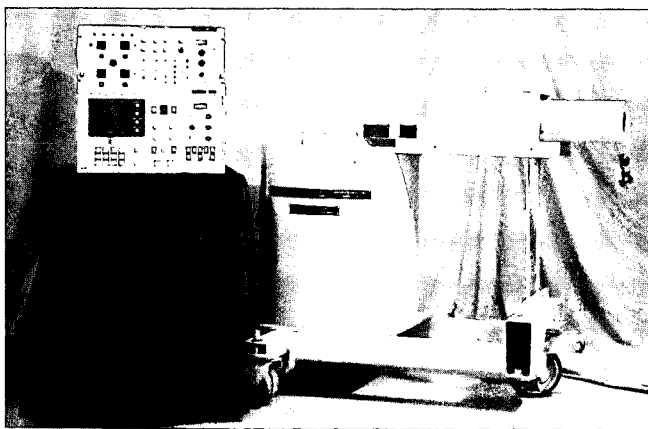


FIGURE 3 PHOTOGRAPH OF MEASURING HEAD AND ELECTRONIC SYSTEM

The sample presentation used in this study consisted of the manual placement of 20 Kg samples (in 28 in. dia. cylindrical holders). A continuous presentation system would consist of a means of transporting a stream of coal having well-defined dimensions (~ 30 cm \times ~ 30 cm cross section) past the measuring heads at approximately 5 to 50 cm/sec. The coal stream could be enclosed suitably (e.g., in a sheet metal tunnel) since the incident neutrons and emitted gamma rays easily penetrate thin engineering materials. Representative sampling and splitting the primary plant streams to yield such an analytical stream is routine in coal engineering.(11)

EXPERIMENTAL RESULTS AND DISCUSSION

Sensitivity studies were made using simulated coal samples consisting of sugar spiked with (1) $\text{MgO} + \text{SiO}_2$, (2) $\text{Fe}_2\text{O}_3 + \text{S}$, (3) $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3$, (4) $\text{CaCO}_3 + \text{NH}_4\text{NO}_3$. In addition unspiked sugar and a sample of $-1/2$ in. bituminous coal were examined. All the samples were measured using each of the four neutron-gamma methods. All the gamma-ray spectra obtained were relatively simple and comprised a few prominent, well-resolved peaks. Thus data analysis consisted simply of integrating each peak and subtracting background measured in a group of adjacent channels. Table II summarizes the results. The neutron-gamma method used in each case is listed along with the sensitivity obtained. Also, typical concentration ranges for these elements in U.S. coals are given. It is seen that the sensitivities obtained are adequate for all the elements tested.

TABLE II
PRELIMINARY RESULTS OF SIMULATED COAL ANALYSIS

Element	Concentration Range in U.S. Coals	Method Used	Gamma-Ray Energy (MeV)	Source	Measurement Time (sec)	Sensitivity (1 Std. Dev.)
H	$\sim 5\%$	Thermal n. Prompt γ	2.23	Cf-252	500	0.01% H
C	65-75%	Fast n. Prompt γ	4.43	Pu-Be	500	0.2% C
N	$\sim 2\%$	Thermal n. Prompt γ	10.32, 10.83	Cf-252	500	0.1% N
Na	0.01-0.2%	$\text{Na}^{23}(\text{n},\gamma)\text{Na}^{24}$ Thermal n. act ⁿ	2.75	Cf-252	300 + 300*	0.01% Na
Al	0.6-2.5%	$\text{Al}^{27}(\text{n},\gamma)\text{Al}^{28}$ Thermal n. act ⁿ	1.78	Cf-252	300 + 300*	0.003% Al
Si	1-6%	$\text{Si}^{28}(\text{n},\text{p})\text{Al}^{28}$ Fast n. act ⁿ	1.78	Pu-Be	300 + 300*	0.05% Si
S	0.2-7%	Thermal n. Prompt γ	5.42	Cf-252	500	0.03% S
Ca	0.1-1.8%	$\text{Ca}^{48}(\text{n},\gamma)\text{Ca}^{49}$ Thermal n. act ⁿ	3.09	Cf-252	300 + 300*	0.1% Ca
Fe	0.4-3%	Thermal n. Prompt γ	7.63	Cf-252	500	0.1% Fe

Neutron-gamma techniques yield linear calibrations of gamma peak area vs element concentration from the detection limit to 100%. This and other work with the same equipment(12) showed that heterogeneity and matrix absorption effects, common in other instrumental analysis techniques, were negligible. One exception to this is thermal neutron absorption caused by increasing hydrogen content of the sample. The effect is proportional to the 2.23 MeV H peak area, and monitoring that peak can yield a satisfactory correction. Alternatively, it is possible to monitor the thermal neutron flux in the sample.

*Activation time plus counting time.

The only other interferences found were peak overlaps in the gamma-ray spectra. These are all readily resolved and present work is concentrated on finding the simplest methods to do this. We have shown that one such interference, between Al and Si, is resolved by using two neutron-gamma techniques. Al and Si activate to the same isotope, Al^{28} , so that neither gamma energy nor time resolution can be used to discriminate between the signals. The dual source technique(13) uses two separate irradiations, by different sources, of similar samples. In one case fast neutrons preferentially excite Si and in the second, thermal neutrons preferentially excite Al. Solution of a pair of simultaneous, linear equations provides accurate Al and Si concentrations. In other interferences, for example, Mn on Al, Si and Cl, Ca on Na, the interfering species emits other gamma rays with a fixed intensity ratio to the interfering one. Measurement of the intensity ratio, which is an instrumental constant, and the intensity of the resolved lines is a straightforward way to correct for this type of interference. A microprocessor-based calculator interfaced to the multichannel analyzer then provides a ready method for solving the linear equations and yielding concentration data suitable for direct digital readout and plant control.

REFERENCES

- (1) Mott, R. A. and Spooner, C. E., Fuel 19, 236-31 and 242-51 (1940).
- (2) Loska, L. and Gorski, L., Koks, Smola, Gaz 18 (2), 52-56 (1973).
- (3) Rhodes, J. R., Daglish, J. C. and Clayton, C. G., "A Coal Ash Monitor with Low Dependence on Ash Composition", in Radioisotope Instruments in Industry and Geophysics I, IAEA, Vienna 1966, pp. 447.
- (4) Rhodes, J. R., Berry, P. F. and Sieberg, R. D., "Nuclear Techniques for On-Stream Analysis of Ores and Coal", ORO-2980-18, USAEC (now USERDA) September 1968.
- (5) Stewart, R. F. et al., "Nuclear Meter for Monitoring the Sulfur Content of Coal Streams", U. S. Bureau of Mines TPR 74 (1974); RI 8038 (1975); and MERC/RI-76/4 (1976).
- (6) Hall, A. W. et al., "Continuous Monitoring of Coal by a Neutron Moisture Meter", U. S. Bureau of Mines RI 7807 (1973).
- (7) Rasmussen, N. C. et al., "The Analysis of Coal Using a Cf-252 Source", Trans. ANS 14 (2) p. 931 (1971); also Trans. ANS 10 (1), p. 29 (1967).
- (8) Parsignault, D. R. et al., "A Prompt Gamma-Ray Coal Analysis System", CONF 710402, Augusta, Ga., 1971, p. IV-40.
- (9) Californium-252 Progress 20, January 1976, p. 37.
- (10) Duffy, D. et al., "Analysis of Synthetic Coals with Capture Gamma-Rays Using Cf252", Trans. ANS 24, p. 117 (1976).
- (11) Hall, D. A., "Automatic Sampling of Coal", Colliery Engineering; Part 1, February 1963, p. 55, Part 2, March 1963, p. 105, Part 3, April 1963, p. 143.
- (12) Taylor, M. C., "A New Method for Field Analysis of Plastic Concrete", CERL Technical Report M-64 (1973).
- (13) Taylor, M. C. and Rhodes, J. R., "Analyzing Process Streams by Neutron Activation--A Dual Source Technique", Instrum. Technol. 21, 32-35, February 1974.